Journal of Magnetism and Magnetic Materials 322 (2010) 197–207

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Grain size refinement and magnetostriction of ferromagnetic shape memory Fe–Pd–Rh alloys

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ARTICLE INFO

Article history:
Received 7 June 2009
Received in revised form
24 August 2009
Available online 4 September 2009

Keywords:
Fe–Pd–Rh alloys
Grain size refinement
SEM and TEM microstructures
Vickers microhardness
Magnetic property

ABSTRACT

This paper reports the forging of bulk ferromagnetic shape memory (FSM) Fe–30Pd–2Rh (at%) alloys to a ~40% reduction in thickness, followed by thermal annealing at 950–1100 °C for various times and quenching in ice brine to induce recrystallization (i.e. grain size refinement). Investigation with the Vickers microhardness test reveals that the process of recrystallization results in increased ductility of the fine grains. TEM and magnetostriction investigations reveal two kinds of twins contained in the strain-forged sample annealed at 950 °C for 3 h, i.e. deformation and transformation twins, and these twins also improved a higher magnetostriction as well as ductility in the alloys that may be useful in magneto-mechanical applications (such as microactuator or spring).

1. Introduction

Deformation of ferromagnetic shape memory (FSM) alloys can be performed by application of a magnetic field, without physical contact. In addition, the response to strain from the magnetic field can be sufficiently quick. As a result, FSM alloys are receiving great attention at present. The main mechanism that results in the field-induced strain in FSM alloys is martensite variant reorientation as a result of magnetic field-induced twin boundary motion. In this mechanism, the magnetocrystalline anisotropy energy of a magnetic field-favored martensite variant is larger than the energy required for twin boundary motion, causing the martensite variant to grow at the expense of others. This results in recoverable magnetic field-induced shape changes, which are attributed to the reorientation of twin structure. Magnetic field control of the shape memory effect was recently suggested as a principle for the operation of a new type of actuator material. A martensitic phase generally accommodates the strain associated with the transformation by the formation of twin variants that pack together in compatible orientations to minimize the strain energy, as the magnetization of a ferromagnet may take on different orientations by breaking up into domains to minimize the magnetostatic energy. Alignment of these twin variants by the motion of twin boundaries can result in large strains. In addition, magnetic field control of the twin-variant orientation requires that the magnetocrystalline anisotropy energy, $K_u=(M_s \times H_a \times \rho)/2$, is sufficient to induce motion of the twin boundaries. Appropriate magnetic field energies E required for driving the actuators are: $K_u > E > E_t+W$ (where K_u denotes the magnetocrystalline anisotropy energy, for an FSM material with high magnetocrystalline anisotropy energy (K_u), it takes less energy to move the twin boundaries to reach a certain strain, and E_t is the energy required for reorienting the twin structure to reach a certain strain) (i.e. energy of twin boundary motion). E_t includes the mechanical work done in the matrix. W denotes the work done by the actuator materials. When the external magnetic field is applied, the magnetization tends to turn from the easy directions of the unit cells to the direction of the external magnetic field. If the magnetocrystalline anisotropy energy (K_u) is high and the energy of twin boundary motion (E_t) is low, the magnetization turns the unit cells of one twin variant into another as the magnetization turns to the direction of the external field. In the meantime, magnetization remains in the easy direction in the turned unit cells. This phenomenon differs from magnetostriction, in which magnetization rotates to the field direction without changing the unit cell orientations [1,22,23]. The mechanism of magnetic field-induced turning of the unit cells of one twin variant into another results in a strain of the actuator material. Currently, there are several FSM materials, such as Fe–Pd–Rh, Fe–Pd, Fe–Pt, and Ni–Mn–Ga alloy systems, based on this mechanism under intensive investigation [1,22,23]. Some of them (such as Ni–Mn–Ga alloys) demonstrate huge strains. For example, the Ni–Mn–Ga single crystal reveals a reversible magnetic field-induced (MFI) strain in the order of 5% at a temperature slightly below the martensitic transformation temperature. However, one of the

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doi:10.1016/j.jmmm.2009.08.046

serious problems in applications of Ni–Mn–Ga FSM alloys is the extreme brittleness in the polycrystalline bulk state, and deformation into a required shape sometimes ends in failure. It is possible to increase the ductility of FSM Fe–30Pd alloys via the addition of rhodium (Rh) to the alloy system, followed by strain-forged deformation and thermal recrystallization to generate grain size reduction. Because recrystallization forms a new set of strain-free and equiaxed grains that have low dislocation densities. The driving force that produces this new grain structure is the difference in the internal energy between the strained and the unstrained material [2]. The new grains form as very small nuclei and grow, until they completely consume the parent material. Thus, recrystallization of strained metals can be used to refine the grain structure that leads to reduced hardness in increased ductility in the material [3]. In addition, grain size reduction of recrystallization has a direct influence on the properties of the metals. For example, fine-grained metals are stronger and tougher than coarse-grained metals. Grain size reduction also influences the magnetostriction of the alloys that could lead to improvements in ferromagnetic shape memory alloys (FSMA), such as Fe–Pd–Rh materials used in magneto-mechanical applications (such as microactuator or spring). In this study, we report the results of an experimental investigation of the influence of annealing temperature and time on recrystallization in generating optimal ultra fine grain sizes (0.5–3.5 μm). The bulk FSM Fe–30Pd–2Rh (at%) alloys were forged to produce a ~40% reduction in thickness. Then thermal annealing at 950–1100 °C for various times was performed to induce recrystallization. The optimal grain size reduction, microstructures, mechanical properties, and magnetic properties of the alloys were studied by scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM), Vickers microhardness test, magnetostriction making use of the strain gauge method, and hysteresis loops using SQUID.

2. Experimental procedures

The Fe–30Pd–2Rh (at%) ferromagnetic shape memory (FSM) alloys used in the study were prepared by melting pure electrolytic iron (99.9%), pure palladium (99.95%), and pure rhodium powder (99.95%) in an arc vacuum furnace under a controlled protective argon atmosphere. Samples were sliced from the cast ingot and sealed in an evacuated quartz capsule, where they were homogenized at 1050 °C for 70 h. After homogenization, they were then subsequently hot- and cold-forged to about ~40% reduction in thickness. After being forged, the specimens were polished and sealed in an evacuated quartz capsule again and annealed at 950–1100 °C for various times, followed by quenching in ice brine. The microstructure observations with SEM were carried out with polished specimens etched in a solution of 60% HCl and 40% HNO_3 at a temperature of about 85 °C. A scanning electron microscopy (SEM), model FEI QUANTA-400F SERIES microscopy, was used to examine the samples with the secondary electron (SE) image and energy dispersive spectroscopy (EDS) function. Thin foils for TEM studies were prepared by double jet electropolishing in a solution containing 75% acetic acid, 15% perchloric acid, and 10% methanol in a temperature range of −7 to 10 °C using a current density of 2–4 A/cm^2. Transmission electron microscopy (TEM), with a double tilt stage, was performed in an analytical type high resolution electron microscopy (Hitachi HF-2000) with a field emission gun operated at 200 kV and a JEM-2100F TEM operated at 200 kV. The X-ray diffraction patterns were detected at room temperature using an X-ray diffractometer (Siemens D5000 Karlsruhe) with Cu–Kα radiation, and the diffraction angles were in the 2θ ranges from 35° to 140°. The Vickers microhardness of the as strain-forged sample and the strain-forged sample after annealing at 950–1100 °C for various times was measured. Vickers microhardness was obtained at a load of 300 g and a time of 20 s using a conventional method. To obtain reliable Vickers microhardness values of various samples, average values were obtained from seven indentations on different parts of each specimen. The magnetostriction measurements were made use of the strain gauge method in association with a magnetostrictive-meter equipment. The magnetic property measurements were carried out with a superconducting quantum interference device (SQUID) magnetometer. The magnetization vs. the magnetic field (M–H) curves for the samples were measured at 50, 100, and 300 K with the maximum applied field of 5000 Oe.

3. Results and discussion

3.1. Microstructure investigations

Fig. 1(a) is an SEM micrograph taken normal to the forged direction of the sample strain-forged to a ~40% reduction in thickness. Indicated by the arrow are strain-induced lamellar structures. The existence of lamellar structures can be ascribed to the anisotropic plastic behavior of lamellar colonies [4]. The strain-forged loading axis (i.e. forging direction) is perpendicular to the lamellar boundaries, so the yield stress is high. In this forging direction, the deformation must propagate through the lamellar interfaces [4,5]. The slip bands, slip steps, and the dislocation cells (or substructures) are clearly discernible. Since the corresponding X-ray diffraction data of the deformed sample reveal the $\{2\,0\,2\}_{L10}$ reflection to be the main diffraction peak, as shown in Fig. 7(a), it can be reasonably inferred from Fig. 1(a) that strain-induced fcc→$L1_0$ phase transformations have taken place on the {2 0 2} plane in the strain-forged sample. The atomic displacements of the strain-forged specimen tend to occur in indistinct, complex, three-dimensional regions in slip bands along the {1 0 1} (i.e. {2 0 2}) planes, which also indicate the large atomic displacement along the $\langle 10\bar{1}\rangle$ direction. The microtwin microstructures in Fig. 1(a) are likely to be strains with $L1_0$ martensite nuclei lying on the {1 0 1} plane of the strain matrix [4,5]. Fig. 1(b) shows an SEM image taken from the areas parallel to the forged direction (i.e. cross-section region). In this direction, the lamellar boundaries are either inclined at an intermediate angle to the loading axis (i.e. the forging direction) or parallel to the loading axis. In the former condition, the lamellar colonies are easily deformed by shear parallel to the interfacial planes, and the yield stress is low. In the latter case, the lamellar boundaries are parallel to the loading axis, and the yield stress is moderately high. The slip bands along the {1 0 1} plane are also clearly observed in the SEM image, as shown in Fig. 1(b), indicated by an arrow.

Fig. 1(c) is a TEM bright field (BF) image taken from the strain-induced lamellar structures. The microstructures of the BF image consist of deformed lamellar grains (and elongated subgrains) containing a high density of dislocations at the grain boundary. A TEM selected area diffraction pattern (SADP) taken from the corresponding BF micrograph is shown in Fig. 1(d). Careful analysis of the SADP reveals the orientation relationship $[\bar{1}\,\bar{1}\,0]_{L10}\|[1\,0\,0]_{L1m}$ (hkl denotes tetragonal $L1_0$ structure and the ordered $L1_0$ martensitic structure with lattice parameters of a=3.869 Å, c=3.696 Å, and c/a=0.955; $\underline{hkl}$ denotes $L1_m$ monoclinic martensitic phase with lattice parameters of a=3.191 Å, b=3.696 Å, c=3.128 Å, and β=91.834°). The $L1_0$ martensite whose c axes (c_{L10}=3.696 Å) are equal to b axes (b_{L1m}=3.696 Å) of the $L1_m$ martensite structure that are formed so as for the elastic strain energy in the adaptive $L1_m$ lattice to be minimized [6,7]. The SADP indicates that two phases exist in the strain-induced lamellar